

(19) **DANMARK**

(10) **DK/EP 1742869 T3**



(12) **Oversættelse af  
europæisk patentskrift**

Patent- og  
Varemærkestyrelsen

- 
- (51) Int.Cl.: **C 01 B 17/765 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2015-05-04**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2015-02-25**
- (86) Europæisk ansøgning nr.: **05716570.6**
- (86) Europæisk indleveringsdag: **2005-04-12**
- (87) Den europæiske ansøgnings publiceringsdag: **2007-01-17**
- (86) International ansøgning nr.: **EP2005003798**
- (87) Internationalt publikationsnr.: **WO2005105666**
- (30) Prioritet: **2004-05-05 DE 102004022506**
- (84) Designerede stater: **AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**
- (73) Patenthaver: **Outotec (Finland) Oy, Rauhalanpuisto 9, 02230 Espoo, Finland**
- (72) Opfinder: **DAUM, Karl-Heinz, Lennebergstrasse 17, 55124 Mainz, Tyskland**  
**RIEDER, Jan, Veilchenweg 3, 65321 Heidenrod, Tyskland**  
**STORCH, Hannes, Hundertmorgenring 34, 64546 Mörfelden-Walldorf, Tyskland**
- (74) Fuldmægtig i Danmark: **Budde Schou A/S, Hausergade 3, 1128 København K, Danmark**
- (54) Benævnelse: **Fremgangsmåde og anlæg til fremstilling af svovlsyre ud fra svovldioxidrige gasser**
- (56) Fremdragne publikationer:  
**EP-A- 0 218 411**  
**WO-A-2004/037719**  
**US-A- 2 180 727**  
**US-A- 3 875 294**  
**US-A- 3 907 979**  
**DATABASE WPI Week 200204 Derwent Publications Ltd., London, GB; AN 2002-032802 XP002269015 & RU 2 174 945 C2 (ARPISHKIN I M) 20 October 2001 (2001-10-20)**



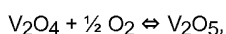
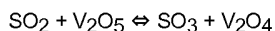
## DESCRIPTION

### Technical Field

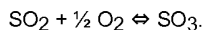
**[0001]** The present invention relates to a process for producing sulfuric acid, oleum or liquid sulfur trioxide, in which a starting gas containing sulfur dioxide at least partly reacts with molecular oxygen in at least one contact with at least one contact stage to form sulfur trioxide, and in which the sulfur-trioxide-containing gas produced is introduced into an absorber and converted to sulfuric acid, and to a corresponding plant.

**[0002]** Conventionally, the production of sulfuric acid is effected by the so-called double absorption process which is described in Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A25, pages 635 to 700. For catalyzing the oxidation of sulfur dioxide to sulfur trioxide, catalysts containing vanadium pentoxide as active component are typically used with an operating range of 380 to 640°C. While an irreversible damage of the catalyst occurs at temperatures above 640°C, the same is inactive at temperatures below 380°C. To avoid a damage of the catalyst, starting gases with a sulfur dioxide content of maximally 13 vol-% are usually charged thereto, as excessive temperatures are obtained in the catalyst bed due to the exothermicity of the oxidation reaction, when gases of a higher concentration are used. The result is that before being charged to the catalyst, gases of a higher concentration must first be diluted with air and/or tonnage oxygen, and correspondingly large gas volumes must be passed through the catalyst. In particular when utilizing pyrometallurgical waste gases as sulfur-dioxide-containing starting gases, which are produced for instance when calcining and melting sulfidic copper and nickel concentrates and typically have a sulfur dioxide content of 20 to 60 vol-%, a great dilution factor thus is necessary. This leads to, disproportionately high investment and operating costs of the sulfuric acid plant.

**[0003]** Beside the temperature, the yield of sulfur trioxide is decisively influenced by the volumetric ratio of sulfur dioxide to oxygen in the starting gas. The partial reactions taking place during the oxidation of sulfur dioxide to sulfur trioxide by means of conventional vanadium pentoxide catalysts can be described in a simplified way by the following formulae:



which corresponds to a total reaction of



**[0004]** According to the principle of Le Châtelier, a higher yield of sulfur trioxide thus can be expected with increasing partial pressure of sulfur dioxide in the starting gas. In practice, a hyperstoichiometric amount of oxygen therefore is used for the oxidation of sulfur dioxide to sulfur trioxide, based on the amount of  $\text{SO}_2$ , namely an amount of  $\text{O}_2$  corresponding to a volumetric ratio  $\text{O}_2/\text{SO}_2$  greater than 0.75, preferably corresponding to a ratio of 1 to 1.2, which corresponds to a volumetric ratio  $\text{SO}_2/\text{O}_2$  of 1:1 to 1:0.83. Therefore, the sulfur-dioxide-containing starting gases, which in general were obtained by combustion of sulfur, must be further diluted with air or tonnage oxygen, apart from the necessity to adjust the sulfur dioxide content to a value below 13 vol-%, also for adjusting a favourable volumetric ratio of  $\text{O}_2$  to  $\text{SO}_2$ , which contributes to the correspondingly large gas volumes to be passed through the catalyst and to the correspondingly high investment and operating costs of conventional sulfuric acid plants.

**[0005]** To overcome these disadvantages, processes for producing sulfuric acid have already been proposed, in which starting gases with a sulfur dioxide content of more than 13 vol-% can be supplied to the catalyst.

**[0006]** Some of these processes provide an alternative catalyst, which can also be operated at temperatures higher than 640°C (WO 99/36175 A1).

**[0007]** DE-OS 20 26 818 discloses a process for the catalytic oxidation of sulfur dioxide to sulfur trioxide in a plurality of contact stages with an intermediate absorption of the sulfur trioxide formed, in which before being introduced into the first contact stage, the starting gases are diluted with dilution air and with sulfur trioxide expelled from oleum to obtain a sulfur dioxide concentration

of 10 to 20 wt-%. What is disadvantageous in this process, however, is the amount of apparatus involved and the technical expenditure necessary for the continuous expulsion of sulfur trioxide from oleum and the comparatively low utilization of the sulfur dioxide in the first contact stage, as only sulfur trioxide is recirculated, but not the reactants sulfur dioxide and oxygen.

**[0008]** To be able to process starting gases with a sulfur dioxide content of 13 to 66 vol-% to sulfuric acid at low cost by using conventional catalysts, DE 102 49 782 A1 proposes a process for producing sulfuric acid, in which from a contact stage upstream of the last main contact stage a partial stream of the gas containing sulfur dioxide and sulfur trioxide is withdrawn, this partial stream is mixed with the starting gas to obtain a contact gas with a sulfur dioxide content of more than 13 vol-% and is recirculated to the first contact stage. As a result of the dilution of the starting gas, comparatively large gas volumes are, however, passed through the catalyst in this process as well.

**[0009]** From US 2,180,727 there is finally known a process for the catalytic conversion of sulfur dioxide to sulfur trioxide with three contact stages, in which a contact gas with a maximum sulfur dioxide concentration of 16 vol-%, a ratio of sulfur dioxide to oxygen of maximally 2.67:1, and a temperature of 412 to 415°C is supplied to the first contact stage, and after the catalytic conversion the sulfur-trioxide-containing process gas withdrawn from the first contact stage is mixed with a corresponding volume of air for cooling and adjusting a hyperstoichiometric oxygen content, before the resulting gas mixture is supplied to the second contact stage and further oxidized therein. The gas leaving the second contact stage is cooled again and, to adjust a hyperstoichiometric ratio of sulfur dioxide to oxygen, mixed with oxygen and supplied to a third contact stage, before the gas leaving the third contact stage finally is supplied to an absorption stage for forming sulfuric acid. However, this process is also limited as regards the maximum concentration of sulfur dioxide in the starting gas supplied to the first contact stage, so that large gas volumes must be passed through the individual contact stages. In addition, the vanadium catalyst used will deteriorate under the chosen process conditions and will become inactive after a certain period.

**[0010]** Document EP 0 218 411 A1 discloses the preparation of sulfur trioxide from sulfur dioxide by catalytic conversion. The gas mixture led to first catalyst stage comprises more than 25 vol-% SO<sub>2</sub>, wherein the maximum molar ratio of sulfur dioxide to oxygen is 4:1. This small ratio of sulfur dioxide to oxygen is generated by adding pure oxygen or oxygen-enriched gas to the gas mixture upstream of its entry into the catalytic converter.

**[0011]** Document US 3,907,971 discloses a plant for the production of sulfuric acid wherein a part of the SO<sub>3</sub> lean cycle gas containing a rest of sulfur trioxide is recycled from the absorption tower to the contact vessel. The SO<sub>3</sub> rich gas leaving the contact stages is led to the subsequent contact stages.

**[0012]** Document WO2004/027719 A1 published after the priority date of the present patent application shows a recirculation of the SO<sub>3</sub> containing gas from the main contact to the pre-contact.

### **Description of the Invention**

**[0013]** Therefore, it is the object of the present invention to provide for the inexpensive production of sulfuric acid on the basis of concentrated starting gases, in particular to provide a process for producing sulfuric acid, in which only small gas volumes must be supplied to the first contact stage, based on the amount of sulfur dioxide used.

**[0014]** In accordance with the invention, this object is solved by a process and a plant comprising the features of claims 1 and 17, respectively.

**[0015]** Preferred embodiments of the invention are evident from the dependent claims.

**[0016]** In accordance with the present invention it could surprisingly be found that the catalytic oxidation of sulfur dioxide to sulfur trioxide with a understoichiometric oxygen content, namely a volumetric ratio SO<sub>2</sub>/O<sub>2</sub> of more than 8:1 or even more than 10:1, can be operated continuously when the starting gas has an SO<sub>2</sub> content of 80 to 99.99 vol-%. The use of normal catalysts containing vanadium pentoxide is possible, a satisfactory yield also being achievable on an industrial scale without damage to the catalyst. Due to the comparatively high SO<sub>2</sub> content on the one hand and the comparatively low oxygen content on the other hand, considerably smaller volumes of starting gas, based on the amount of SO<sub>2</sub>, are supplied to the first contact stage in the process of the invention as compared to the prior art. The investment costs for the plant required for performing the process thereby are reduced considerably. In particular, this amount of 50 to 150 liters/daily ton of starting gas compared with the conventionally required amount of 160 to 250 liters/daily ton of starting gas requires a substantially lower specific quantity of

catalyst. The displacement of the equilibrium of the oxidation reaction as a result of the high SO<sub>2</sub> content on the part of the products is compensated by the understoichiometric oxygen content, based on the amount of SO<sub>2</sub>, which displaces the thermodynamic equilibrium of the oxidation reaction on the part of the educts. By correspondingly adjusting the SO<sub>2</sub> content on the one hand and the volumetric ratio SO<sub>2</sub>/O<sub>2</sub> on the other hand, the temperature in the contact stage thus can be adjusted to a value below the temperature that leads to an irreversible damage of the catalyst, in the case of the use of vanadium pentoxide to a temperature of maximally 640°C, and an overheating of the catalyst thus can be avoided.

**[0017]** The contact gas supplied to the first contact stage has a sulfur dioxide content of 80 to 99.99 vol-%, in particular preferably more than 90 vol-%. In this way, the amounts of contact gas to be supplied to the first contact stage, based on the amount of SO<sub>2</sub>, are particularly low.

**[0018]** To avoid an irreversible damage of the catalyst as a result of overheating, the volumetric ratio of SO<sub>2</sub> to oxygen of the contact gas supplied to the first contact stage, in dependence on the amount of SO<sub>2</sub>, is more than 8:1, and highly preferably more than 10:1.

**[0019]** In principle, all concentrated gas mixtures containing sulfur dioxide and oxygen, which were produced in any way known to those skilled in the art, for instance corresponding gases produced in pyrometallurgical plants, can be used as starting gases in the process of the invention. In particular gas mixtures obtained by combustion of elementary sulfur with tonnage oxygen, which preferably has an oxygen content of at least 95 to 98 vol-%, preferably those with a sulfur dioxide content of 80 to 99.99 vol-%, an oxygen content of 0.01 to 10 vol-%, and a content of molecular nitrogen or other inert gases of 0 to maximally 10 vol-%, and particularly preferably those with a sulfur dioxide content of 90 to 95 vol-%, an oxygen content of 3 to 7 vol-%, and with a content of molecular nitrogen or other inert gases of 0 to maximally 5 vol-%, or gas mixtures of the same composition, which were produced by other processes, turned out to be useful as starting gases. The same can be supplied to the first contact stage undiluted or upon dilution with air or preferably tonnage oxygen for adjusting a suitable volumetric ratio SO<sub>2</sub>/O<sub>2</sub> and a suitable SO<sub>2</sub> content. A particular advantage of this embodiment consists in that due to the absence or the low content of molecular nitrogen in the contact gas, the sulfuric acid obtained with the process of the invention contains no nitrogen oxide (NO<sub>x</sub>) impurities or at least, compared with the processes known in accordance with the prior art, in which air with an N<sub>2</sub> content of about 79 vol-% is used as combustion gas, contains nitrogen oxide (NO<sub>x</sub>) impurities reduced by one order of magnitude. Accordingly, in dependence on the purity of the tonnage oxygen used for the combustion of sulfur and/or of the tonnage oxygen possibly used for diluting the sulfur-dioxide-containing starting gas, no or at best very small amounts of waste gas are produced, so that the specific emissions, based on the amount of sulfuric acid formed, are substantially lower as compared to the conventional processes. Furthermore, no drying tower for drying the ambient air is required for performing the process of the invention, if no dilution gas or tonnage oxygen is used as dilution gas instead of air.

**[0020]** In principle, any catalyst known to those skilled in the art as useful for oxidizing sulfur dioxide to sulfur trioxide can be used in the process of the invention. Good results are obtained in particular with conventional catalysts containing vanadium pentoxide. What has also been used quite successfully are iron-containing catalysts, in particular granular catalysts comprising a porous supporting material, preferably with a BET surface area of 100 to 2000 m<sup>2</sup>/g and an SiO<sub>2</sub> content of at least 90 wt-% and an active component containing 10 to 80 wt-% iron, the weight ratio of supporting material to active component particularly preferably lying in the range from 1 to 100.

**[0021]** In the case of catalysts containing vanadium pentoxide, for instance, an inlet temperature of the contact gas into the first contact stage of about 450°C, in particular of about 470°C and most preferably about 500°C turned out to be particularly useful. When using granular catalysts comprising a porous supporting material of SiO<sub>2</sub> with an active component containing 10 to 80 wt-% iron, the inlet temperature in this catalyst preferably is about 500°C, particularly preferably about 520°C and quite particularly preferably about 540°C.

**[0022]** Preferably, the contact gas is supplied to the first contact stage with a pressure of 1 to 30 bar, and particularly preferably with a pressure of 3 to 12 bar. In this way, the amount of gas actually supplied to the first contact stage is further reduced on the one hand, and on the other hand the thermodynamic equilibrium of the oxidation reaction is displaced on the part of SO<sub>3</sub> because of the elevated pressure. Since the yield of SO<sub>3</sub> in particular depends on four parameters, namely the temperature, the pressure, the amount of SO<sub>2</sub> and the ratio SO<sub>2</sub>/O<sub>2</sub> in the first contact stage, satisfactory yields of sulfur trioxide can be obtained even with a particularly high ratio SO<sub>2</sub>/O<sub>2</sub> due to the elevated pressure. In this embodiment, it has also turned out to be expedient to produce the starting gas already under the chosen pressure, in that for instance during the combustion of elementary sulfur both the liquid sulfur and the tonnage oxygen used for combustion and/or the used combustion air are supplied to the combustion chamber with

the indicated pressure and the combustion chamber is operated at this pressure. The advantage is that the sulfuric acid plant requires no gas blower for conveying the process gases through the contact and absorption stages.

**[0023]** To avoid an irreversible damage of the catalyst during operation of the first contact stage, the sulfur dioxide content, the volumetric ratio  $\text{SO}_2/\text{O}_2$ , the inlet pressure and the inlet temperature of the contact gas supplied to the first and all succeeding contact stages are chosen such that in the contact stage a temperature is obtained, which lies below the temperature that leads to a damage of the catalyst, but above the operating temperature of the catalyst. In the case of a catalyst containing vanadium pentoxide, the upper limit of the temperature to be adjusted is about  $640^\circ\text{C}$ , and the lower limit is about  $380^\circ\text{C}$ .

**[0024]** In accordance with a first embodiment of the present invention, further contact stages, preferably 2 to 4 further contact stages, are provided downstream of the first contact stage, the individual contact stages being combined to one or more, preferably one or two contacts. Downstream of each contact, an absorber can be provided, in which sulfur trioxide is at least partly, preferably completely removed from the process gas and converted to sulfuric acid, liquid  $\text{SO}_3$  or oleum in a manner known to those skilled in the art. The sulfur-trioxide-containing process gas leaving the first to penultimate contact stages is mixed with oxygen for adjusting a suitable ratio  $\text{SO}_2/\text{O}_2$  and cooled to an inlet temperature suitable for the next contact stage, before it is supplied to the respectively succeeding contact stage for further oxidation. The adjustment of the necessary inlet temperature into the respectively succeeding contact stage can be achieved by adding correspondingly tempered oxygen-containing gas, for instance liquefied  $\text{O}_2$ , and/or by means of a heat exchanger. It is mostly necessary to also operate the second and/or the succeeding contact stages with a contact gas with a understoichiometric oxygen content, based on the  $\text{SO}_2$  content. The process gas leaving the last contact stage is supplied to an absorber, in which sulfur trioxide is removed from the process gas by forming sulfuric acid, liquid  $\text{SO}_3$  or oleum, and the resulting waste gas can, if necessary, be removed via a chimney, for instance after a chemical posttreatment in a gas washing plant operated e.g. with hydrogen peroxide, or be supplied to a further treatment in the sulfuric acid plant.

**[0025]** In accordance with a second embodiment of the present invention it is likewise provided that downstream of the first contact stage further contact stages, preferably 2 to 4 contact stages, are disposed, which are preferably combined to one or two contacts, but that a partial stream of the contact gas leaving the first contact stage and/or one or more of the succeeding contact stages is withdrawn and this partial stream or these partial streams is/are mixed with the starting gas before the same enters the first contact stage. In this way, the sulfur dioxide content and the ratio  $\text{SO}_2/\text{O}_2$  of the starting gas can be adjusted to a suitable value for the first contact stage. On the other hand, this results in a better utilization of energy, as the recirculation of the thermal energy of the recirculated, partly converted and hot process gas is utilized for preheating the starting gases. As a result, this procedure requires correspondingly smaller heat exchangers. In accordance with the invention, however, only such amounts of process gas are recirculated, which provide a contact gas supplied to the first contact stage with a sulfur dioxide content of more than 16 vol-% and with a volumetric ratio of sulfur dioxide to oxygen of more than 2.67:1.

**[0026]** As an alternative, it is also possible to withdraw and recirculate the partial stream or the partial streams not directly at the outlet of the respective contact stages, but only after the intermediate or final absorption stages, so that less sulfur trioxide, which displaces the thermodynamic equilibrium of the oxidation reaction on the part of the educts, is introduced into the contact gas to be supplied to the first contact stage.

**[0027]** Furthermore, instead of being recirculated to the gas to be supplied to the first contact stage, the partial stream withdrawn from a contact stage and/or from the first intermediate absorber can also be supplied to the gas (air or preferably tonnage oxygen) used for the combustion of sulfur for producing the sulfur-dioxide-containing starting gas and/or directly to the sulfur burner. As those skilled in the art will recognize, it is of course also possible to combine the aforementioned alternatives in any way, for instance to supply one part of the partial stream to the gas to be supplied to the first contact stage and the other part of the partial stream to the gas used for the combustion of the elementary sulfur.

**[0028]** Finally, in accordance with a third embodiment of the present invention, the process can be operated with only one contact, which preferably consists of 1 to 3 contact stages, wherein preferably at least part of the process gas leaving the contact and/or the absorber downstream of the contact is withdrawn and recirculated to the starting gas to be supplied to the first contact stage and/or to the combustion gas to be supplied to the combustion of sulfur and/or directly into the sulfur burner.

**[0029]** Preferably, the partial stream or partial streams in accordance with the second and third embodiments of the invention, which was/were mixed with the starting gas before entrance thereof into the first contact stage, is/are dimensioned such that the contact gas supplied to the first contact stage consists of 90 to 95 vol-% sulfur dioxide, 3 to 7 vol-% oxygen, 0.01 to 5 vol-% sulfur trioxide and 0 to maximally 5 vol-% nitrogen or another inert gas.

[0030] Furthermore, the present invention relates to a plant for producing sulfuric acid, liquid SO<sub>3</sub> or oleum from gases rich in sulfur dioxide, which can be used in particular for performing the process of the invention.

[0031] In accordance with the invention, the plant includes at least one contact with a least one contact stage for reacting a starting gas containing SO<sub>2</sub> with oxygen to obtain SO<sub>3</sub>, and at least one absorber, wherein the inlet region of the first contact stage is connected with the outlet region of one or more contact stages and with the outlet region of one or more absorbers via one or more recirculation conduit(s).

[0032] Preferably, the at least one recirculation conduit leads from the outlet region of the first contact to the inlet region of the first contact stage.

[0033] In accordance with a development of the invention it is proposed that the plant includes 3 to 5 contact stages, which particularly preferably are combined in one or two contacts. In principle, the individual contact stages can include any catalyst material known to those skilled in the art for this purpose. Preferably, however, conventional catalysts are provided, for instance those on the basis of vanadium pentoxide with or without addition of caesium, or on the basis of other metal oxides such as iron oxide.

[0034] In accordance with a particular embodiment of the present invention, the plant additionally includes a sulfur burner with a combustion chamber for the combustion of elementary sulfur with tonnage oxygen or air, the sulfur burner and/or the inlet region of the combustion chamber being connected with the outlet region of one or more contact stages and/or with the outlet region of one or more absorbers.

[0035] The invention will subsequently be explained in detail with reference to embodiments and the drawing. All features described and/or illustrated in the Figures form the subject-matter of the invention, independent of their inclusion in the claims or their back-reference.

#### **Brief Description of the Drawings**

##### **[0036]**

Fig. 1

shows a process diagram of a process and a plant in accordance with the prior art;

Fig. 2

shows a process diagram of a process and a plant in accordance with the prior art;

Fig. 3

shows a process diagram of a process and a plant in accordance with a first embodiment of the present invention;

Fig. 4

shows a process diagram of a process and a plant in accordance with a second embodiment of the present invention;

Fig. 5

shows a process diagram of a process and a plant in accordance with a third embodiment of the present invention.

#### **Detailed Description of the Preferred Embodiments**

[0037] The conventional plant as shown in Fig. 1 for producing sulfuric acid in accordance with the prior art, as it is described for instance in Ullmann's Encyclopedia of Industrial Chemistry, comprises a sulfur burner 1, two contacts 2, 3, an intermediate absorber 4 and a final absorber 5. While the first contact 2 (primary contact) includes three contact stages (catalyst layers) 6<sub>1</sub> to 6<sub>3</sub>, which each have a catalyst on the basis of vanadium pentoxide, the second contact 3 (secondary contact) includes two contact stages 6<sub>4</sub>, 6<sub>5</sub>. Between the individual contact stages 6<sub>1</sub> to 6<sub>5</sub>, there is each disposed an intermediate cooler (not shown), in which the process gas leaving the preceding contact stage 6<sub>1</sub> to 6<sub>4</sub> is cooled down to a temperature suitable for entrance into the respectively next contact stage 6<sub>2</sub> to 6<sub>5</sub>.

[0038] In the sulfur burner 1, starting gas with less than 13 vol-%, usually with 10 to 12 vol-% sulfur dioxide and with a volumetric

ratio  $\text{SO}_2/\text{O}_2$  of about 1:1 to 1:0.83 is produced by combustion of elementary sulfur with air. For this purpose, elementary sulfur, generally in liquid form with a temperature of 140 to 150°C, is continuously supplied to the sulfur burner 1 via supply conduit 7, and air which has possibly been dried in advance in a drying tower (not shown) is supplied via supply conduit 8, wherein the hyperstoichiometric oxygen content in the resulting starting gas is controlled by the amount of air introduced into the sulfur burner and/or adjusted by the subsequent addition of dilution air. Via conduit 9, the starting gas is passed through a heat exchanger (not shown), in which the same is preheated to the inlet temperature of the first contact stage 6<sub>1</sub> and is subsequently supplied to the first contact stage 6<sub>1</sub>, before the gas mixture is sequentially passed through the three contact stages 6<sub>1</sub> to 6<sub>3</sub> of the first contact 2 for oxidation. Gas leaving the first contact 2 is supplied to the intermediate absorber 4 via conduit 10 and brought in contact with aqueous sulfuric acid, a large part of the sulfur trioxide formed in the first contact being absorbed by forming sulfuric acid. Subsequently, the remaining gas is supplied to the second contact 3 via conduit 11 and sequentially passed through its two contact stages 6<sub>4</sub> and 6<sub>5</sub>. Gas leaving the second contact 3 is supplied via conduit 12 to the final absorber 5, in which the sulfur trioxide formed is converted to sulfuric acid. While the waste gas is discharged from the plant via the chimney 13, the sulfuric acid produced in the intermediate absorber 4 and in the final absorber 5 is combined and discharged from the plant as a single mass flow via the product discharge conduit 14.

**[0039]** As can be taken from Fig. 2, the plant comprises the components of the conventional apparatus described above, which for the sake of simplicity are provided with the same reference numerals, and in addition includes a plurality of supply conduits 8, 15, 16 for tonnage oxygen, which lead into the sulfur burner 1, the gas supply conduit 9 and the gas conduits provided between the contact stages 6<sub>1</sub> and 6<sub>2</sub> as well as 6<sub>2</sub> and 6<sub>3</sub>, respectively.

**[0040]** In the process of the invention, in contrast to the prior art, a contact gas with a sulfur dioxide content of  $\geq 80$  vol-% and with a volumetric ratio of sulfur dioxide to oxygen of more than 8:1 is supplied to the first contact stage. In the process performed as shown in Fig. 2, this contact gas is produced in that elementary sulfur is continuously introduced into the sulfur burner 1 via supply conduit 7, and tonnage oxygen as combustion gas is introduced via the supply conduits 16 and 8. By adjusting the amount of tonnage oxygen supplied to the sulfur burner 1 per unit of time, based on the amount of elementary sulfur, the sulfur dioxide content of the resulting gas can be adjusted to the desired value, which is more than 80 vol-% and particularly preferably more than 90 vol-%.

**[0041]** The highly concentrated gas produced is withdrawn from the sulfur burner 1 via conduit 9, and its oxygen content, based on the sulfur dioxide content, is possibly adjusted to a desired value by means of tonnage oxygen supplied via conduit 15, preferably to a volumetric ratio of sulfur dioxide to oxygen of more than 8:1 and highly preferably more than 10:1. Subsequently, the gas mixture thus produced is passed through a heat exchanger (not shown), in which it is heated to the suitable inlet temperature of the first contact stage 6<sub>1</sub>, in the case of a catalyst comprising vanadium pentoxide preferably to about 450°C and particularly preferably to about 470°C, and supplied to the first contact stage 6<sub>1</sub>. To avoid a damage of the catalyst in the case of a continuous operation of the plant, the sulfur dioxide content, the volumetric ratio  $\text{SO}_2/\text{O}_2$ , the inlet pressure and the inlet temperature of the contact gas supplied to the first contact stage 6<sub>1</sub> and to the succeeding contact stages 6<sub>2</sub> to 6<sub>5</sub> are chosen such that in the respective contact stage a temperature is obtained, which lies below the temperature that leads to a damage of the catalyst, but above the operating temperature of the catalyst.

**[0042]** Upon cooling, process gas withdrawn from the first contact stage 6<sub>1</sub> is mixed with tonnage oxygen supplied via conduit 16 for adjusting a volumetric ratio  $\text{SO}_2/\text{O}_2$  suitable for the second contact stage 6<sub>2</sub>, which in dependence on the  $\text{SO}_2$  content of the process gas can correspond to a understoichiometric or hyperstoichiometric oxygen content, and is possibly supplied to an intermediate cooler, the optimum volumetric ratio depending in particular on the  $\text{SO}_2$  content of the process gas and on the inlet pressure and the inlet temperature of the second contact stage 6<sub>2</sub>.

**[0043]** Due to the comparatively high  $\text{SO}_2$  content on the one hand and the comparatively low oxygen content, based on the  $\text{SO}_2$  content, on the other hand, considerably smaller volumes of starting gas, based on the amount of  $\text{SO}_2$ , are supplied to the first contact stage in this process as compared to the known processes of the prior art, which on the whole results in considerably lower investment costs as compared to the conventional processes. In particular, a significantly lower specific quantity of catalyst is required as a result thereof.

**[0044]** In contrast to the apparatus shown in Fig. 2, the plant illustrated in Fig. 3 includes a plurality of recirculation conduits 15, 17, 18, of which two recirculation conduits 17 each lead from the outlet of the third contact stage 6<sub>3</sub> and the outlet of the fifth contact stage 6<sub>5</sub> to the gas conduit 9 leading to the first contact stage 6<sub>1</sub>, and of which two recirculation conduits 18 each lead from the outlet of the intermediate absorber 4 and the outlet of the final absorber 5 to the sulfur burner 1, and via each of which a



partial stream of the process gas is recirculated. In addition, via the recirculation conduit 15 leading from the outlet of the sulfur burner 1 to the gas conduit 18, a partial stream of the SO<sub>2</sub>-containing starting gas is recirculated to the sulfur burner 1.

**[0045]** By means of the recirculation of the process gases, a better utilization of energy is achieved as compared to the conventional processes, as hereby the thermal energy of the recirculated, partly converted and hot process gases is utilized for preheating the starting gases and/or the sulfur burner 1, so that merely a correspondingly smaller amount of thermal energy must be supplied externally. Apart from this, the recirculation of partial process gas streams withdrawn from the outlet of the two contacts 2, 3, which apart from SO<sub>2</sub> and O<sub>2</sub> also contain SO<sub>3</sub>, effects a greater variability in terms of process control. This is connected with the fact that SO<sub>3</sub> displaces the thermodynamic equilibrium of the oxidation reaction on the part of the products, so that in this embodiment a total of five parameters, namely the inlet temperature, the inlet pressure, and the SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub> contents, are available for controlling the temperature in the first contact stage 6<sub>1</sub>. Finally, the recirculation of the process gases also contributes to a greater yield. In accordance with the invention, however, only such amounts of process gas are recirculated, which provide a contact gas supplied to the first contact stage with a sulfur dioxide content of  $\geq 80$  vol-% and with a volumetric ratio of sulfur dioxide to oxygen of more than 6:1.

**[0046]** In contrast to the apparatus shown in Fig. 3, the plant illustrated in Fig. 4 includes only one contact 2, which consists of the three contact stages 6<sub>1</sub> to 6<sub>3</sub>, as well as an absorber 5. In addition, this embodiment includes only one recirculation conduit 18 extending from the outlet of the absorber 5, which via the partial conduit 18' leads to the inlet conduit 9 for the first contact stage 6<sub>1</sub> and via the partial conduit 18" to the sulfur burner 1. Due to the only one contact 2, the plant is correspondingly compact and inexpensive. A yield of nevertheless approximately 100%, even with the use of highly concentrated starting gases, based on the amount of SO<sub>2</sub>, for instance those with an SO<sub>2</sub> content of more than 90 vol-%, can be achieved by a correspondingly high degree of recirculation.

**[0047]** The process diagram shown in Fig. 5 differs from the one shown in Fig. 4 in that beside a recirculating conduit 18 leading from the outlet of the absorber 5 into the sulfur burner 1 there are provided three recirculation conduits 17 extending from the outlet of the individual contact stages 6<sub>1</sub> to 6<sub>3</sub>, which converge to one collecting conduit and lead to the inlet conduit 9. By providing a recirculation conduit 17 after each contact stage 6<sub>1</sub> to 6<sub>3</sub>, an even greater variability of the process is achieved in terms of process control.

**List of reference numerals:**

**[0048]**

- 1 sulfur burner
- 2 first contact (primary contact)
- 3 second contact (secondary contact)
- 4 intermediate absorber
- 5 final absorber
- 6 contact stage
- 7 sulfur supply conduit
- 8 supply conduit for combustion gas
- 9 supply conduit to the first contact
- 10 gas conduit to the intermediate absorber
- 11 supply conduit to the second contact

12	conduit to the final absorber
13	chimney
14	product discharge conduit
15	bypass conduit
16	supply conduit for tonnage oxygen
17	recirculation conduit
18	recirculation conduit

## REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

### Patent documents cited in the description

- [WO9936175A1](#) [0006]
- [DEOS2026818](#) [0007]
- [DE10249782A1](#) [0008]
- [US2180727A](#) [0009]
- [EP0218411A1](#) [0010]
- [US3907971A](#) [0011]
- [WO2004027719A1](#) [0012]

### Non-patent literature cited in the description

- Ullmann's Encyclopedia of Industrial Chemistryvol. A25, 635-700 [0002]

**PATENTKRAV**

1. Fremgangsmåde til fremstilling af svovlsyre, oleum eller flydende svovltrioxid, ved hvilken en udgangsgas, der indeholder svovldioxid, i det mindste delvis reagerer med  
5 molekylært oxygen i mindst én kontakt (2, 3) med mindst ét kontaktrin (6<sub>1</sub>) til dannelse af svovltrioxid, og ved hvilken den frembragte svovltrioxidrige gas indføres i en absorber (4, 5) og der omdannes til svovlsyre, **kendetegnet ved, at** en kontaktgas med et svovldioxidindhold på 80 til 99,99 rumfangs%, med et oxygenindhold på 0,01 til 10 rumfangs% og med et volumetrisk forhold mellem svovldioxid og oxygen på mere  
10 end 8:1 tilføres til det første kontaktrin (6<sub>1</sub>).
2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** den til det første kontaktrin (6<sub>1</sub>) tilførte kontaktgas har et svovldioxidindhold på mere end 90 rumfangs%.
- 15 3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** det volumetriske forhold mellem svovldioxid og oxygen i den til det første kontaktrin (6<sub>1</sub>) tilførte kontaktgas er mere end 10:1.
4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** den til det første kontaktrin (6<sub>1</sub>) tilførte kontaktgas består af 90 til  
20 95 rumfangs% svovldioxid, 3 til 7 rumfangs% oxygen og 0 til maksimalt 5 rumfangs% nitrogen eller anden indifferent gas.
5. Fremgangsmåde ifølge krav 4, **kendetegnet ved, at** kontaktgassen fremstilles ved  
25 forbrænding af elementært svovl med teknisk oxygen.
6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** det første kontaktrin (6<sub>1</sub>) omfatter en katalysator, der indeholder vanadium-  
pentoxid.  
30
7. Fremgangsmåde ifølge krav 6, **kendetegnet ved, at** kontaktgassen tilføres til det første kontaktrin (6<sub>1</sub>), som omfatter en katalysator, der indeholder vanadiumpentoxid, med en temperatur på mindst 450°C og særlig foretrukket mindst 470°C.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** kontaktgassen tilføres til det første kontaktrtrin (6<sub>1</sub>) med et tryk på 1 til 30 bar, særlig foretrukket 3 til 12 bar.
- 5 9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** svovldioxidindholdet, det volumetriske forhold SO<sub>2</sub>/O<sub>2</sub>, indgangstrykket og indgangstemperaturen for den til det første kontaktrtrin (6<sub>1</sub>) tilførte kontaktgas vælges således, at der i det kontaktrtrin (6<sub>1</sub>) opnås en temperatur, som er under den temperatur, der ville føre til skade på katalysatoren, men over katalysatorens drifts-  
10 temperatur.
10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** der efter det første kontaktrtrin (6<sub>1</sub>) er tilvejebragt 2 til 4 yderligere kontaktrtrin (6<sub>2</sub>, 6<sub>3</sub>, 6<sub>4</sub>, 6<sub>5</sub>), som fortrinsvis er kombineret til én eller to kontakter (2, 3).
- 15 11. Fremgangsmåde ifølge krav 10, **kendetegnet ved, at** den procesgas, der forlader det første til det næstsidste kontaktrtrin (6<sub>1</sub>, 6<sub>2</sub>, 6<sub>3</sub>, 6<sub>4</sub>), blandes med oxygen, eventuelt efter passage gennem en mellemabsorber (4), indstilles til en for det næste kontaktrtrin (6<sub>2</sub>, 6<sub>3</sub>, 6<sub>4</sub>, 6<sub>5</sub>) egnet indgangstemperatur og tilføres til det pågældende næste  
20 kontaktrtrin (6<sub>2</sub>, 6<sub>3</sub>, 6<sub>4</sub>, 6<sub>5</sub>).
12. Fremgangsmåde ifølge krav 10 eller 11, **kendetegnet ved, at** den procesgas, der forlader det sidste kontaktrtrin (6<sub>5</sub>), tilføres til en absorber (5).
- 25 13. Fremgangsmåde ifølge et hvilket som helst af kravene 10 til 12, **kendetegnet ved, at** der fra den procesgas, der forlader det første kontaktrtrin (6<sub>1</sub>), og/eller fra én eller flere af de procesgasser, der forlader det andet til det sidste kontaktrtrin (6<sub>2</sub>, 6<sub>3</sub>, 6<sub>4</sub>, 6<sub>5</sub>), udtages mindst én delstrøm, og denne delstrøm blandes med udgangsgassen, inden denne kommer ind i det første kontaktrtrin (6<sub>1</sub>), og/eller med den forbrændingsgas, der  
30 anvendes til forbrænding af elementært svovl til fremstilling af den svovldioxidrige udgangsgas, og/eller tilføres direkte til svovlbrænderen (1).
14. Fremgangsmåde ifølge et hvilket som helst af kravene 10 til 12, **kendetegnet ved, at** der fra den procesgas, der forlader mellemabsorberen (4) og/eller slutabsorberen  
35 (5), udtages mindst én delstrøm, og denne delstrøm blandes med udgangsgassen, inden denne kommer ind i det første kontaktrtrin (6<sub>1</sub>), og/eller med den forbrændings-

gas, der anvendes til forbrænding af elementært svovl til fremstilling af den svovldioxidholdige udgangsgas, og/eller tilføres direkte til svovlbrænderen (1).

15. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 9, **kendetegnet ved, at**  
5 der kun er tilvejebragt én kontakt (2) med efterstillet absorber (5), at der fra den procesgas, der forlader et kontakttrin ( $6_1$ ,  $6_2$ ,  $6_3$ ), udtages en delstrøm før og/eller efter absorptionstrinnet (5), og at denne delstrøm blandes med udgangsgassen, inden denne kommer ind i det første kontakttrin ( $6_1$ ), og/eller med den forbrændingsgas, der anvendes til forbrænding af elementært svovl til fremstilling af den svovldioxidholdige  
10 udgangsgas, og/eller tilføres direkte til svovlbrænderen (1).

16. Fremgangsmåde ifølge et hvilket som helst af kravene 10 til 15, **kendetegnet ved, at**  
15 den til det første kontakttrin ( $6_1$ ) tilførte kontaktgas består af 90 til 95 rumfangs% svovldioxid, 3 til 7 rumfangs% oxygen, 0,01 til 5 rumfangs% svovltrioxid og 0 til maksimalt 5 rumfangs% nitrogen eller anden indifferent gas.

17. Anlæg til fremstilling af svovlsyre, oleum eller flydende svovltrioxid, især til udførelse af en fremgangsmåde ifølge et hvilket som helst af kravene 1 til 16, med mindst én kontakt (2, 3), der omfatter mindst ét kontakttrin ( $6_1$ ) til omsætning af en  
20 svovldioxidholdig udgangsgas med oxygen for at opnå svovltrioxid, og mindst én absorber (5), **kendetegnet ved, at** det første kontakttrins ( $6_1$ ) indløbsområde er forbundet med udløbsområdet for ét eller flere kontakttrin ( $6_1$ ,  $6_2$ ,  $6_3$ ,  $6_4$ ,  $6_5$ ) og/eller med udløbsområdet for én eller flere absorbere (4, 5) gennem ét eller flere tilbageføringskredsløb (17, 18), og at en svovlbrænder (1) med et forbrændingskammer til  
25 forbrænding af elementært svovl med teknisk oxygen eller luft er forbundet med udløbsområdet for ét eller flere kontakttrin ( $6_1$ ,  $6_2$ ,  $6_3$ ,  $6_4$ ,  $6_5$ ) og/eller med udløbsområdet for én eller flere absorbere (4, 5).

18. Anlæg ifølge krav 17, **kendetegnet ved, at** mindst ét tilbageføringskredsløb (17,  
30 18) fører fra udløbsområdet for den første kontakt (2) til indløbsområdet for det første kontakttrin ( $6_1$ ).

19. Anlæg ifølge krav 17 eller 18, **kendetegnet ved, at** det omfatter 3 til 5 kontakttrin ( $6_1$ ,  $6_2$ ,  $6_3$ ,  $6_4$ ,  $6_5$ ), fortrinsvis kombineret i én eller to kontakter (2, 3).

DRAWINGS

Fig.1

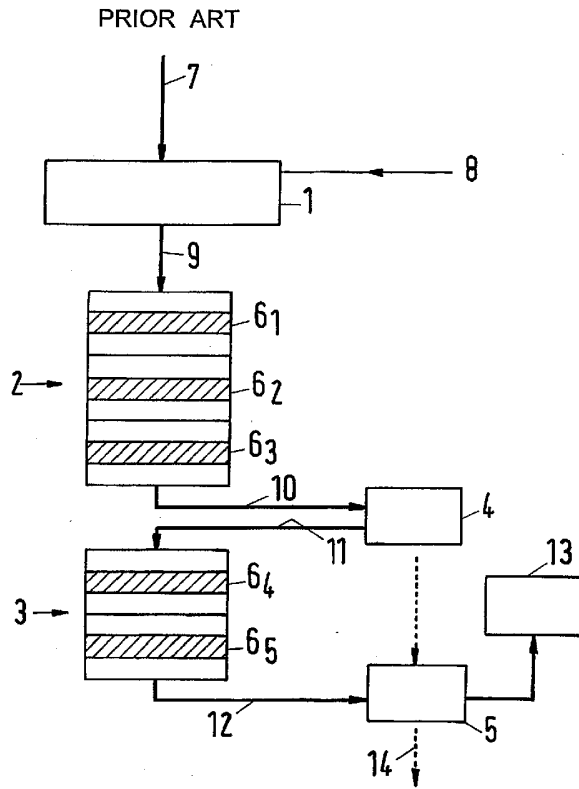


Fig.2

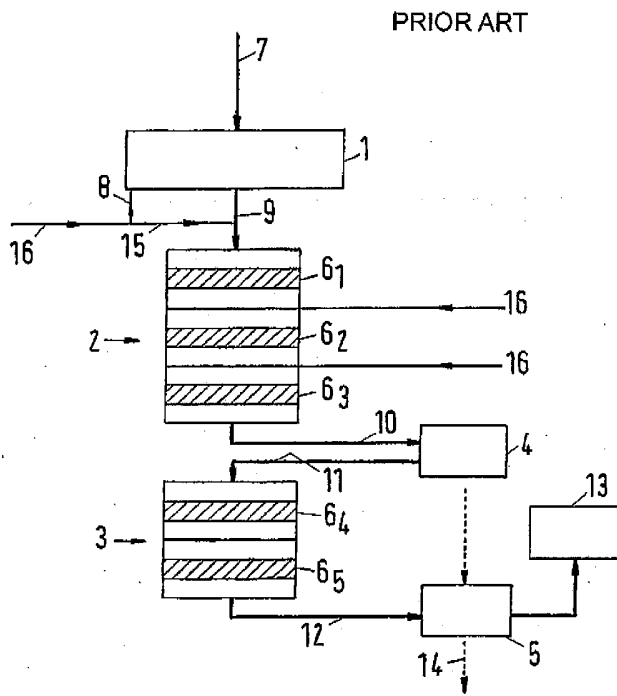






Fig.4

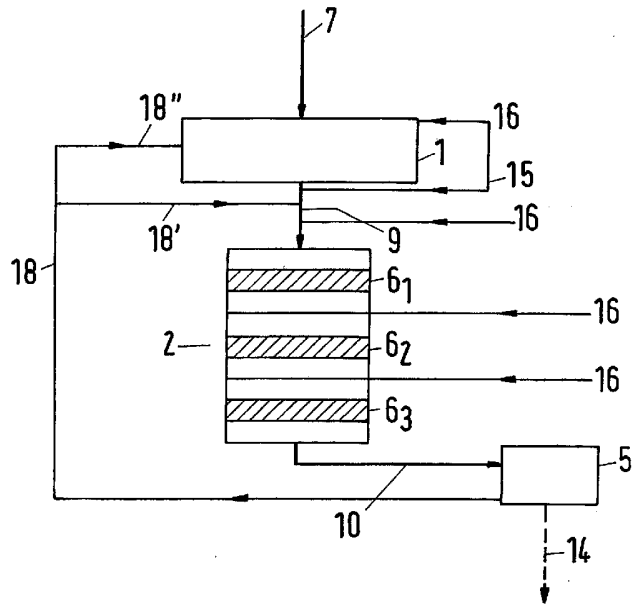


Fig.5

